

# IN-SITU $^1\text{H}$ NMR STUDY OF FLUIDITY ENHANCEMENT BY HYDROGEN-DONOR AND NON-DONOR PITCHES FOR A BITUMINOUS COAL

M. Mercedes Maroto-Valer, John M. André sen and Colin E. Snape

University of Strathclyde, Department of Pure and Applied Chemistry,  
295 Cathedral Street, Glasgow G1 1XL, Scotland, UK

*Keywords:* Hydrogen-donor, pitch, fluid phase, high temperature  $^1\text{H}$  NMR.

Hydrogen-donor ability has been ascribed as one of the factors responsible for the stabilisation of the plastic phase during coal carbonisation. In-situ high temperature  $^1\text{H}$  NMR has been used here to quantify the interactions between a low-volatile bituminous coal and both a normal coal tar pitch (CTP) and a hydrogen-donor pitch (HDP) obtained from a coal liquefaction process. When the CTP was added to the coal (25% w/w, 150-250  $\mu$ ), the amount of fluid material increased by nearly 20% more than that predicted at maximum fluidity close to 450°C. Indeed, a larger synergistic effect was observed with the HDP. By 400°C, 90% of the fluid phase concentration observed at 450°C had already been generated, corresponding to an enhancement of 50% over that predicted. However, particle size appears to be a dominant factor under the slow heating regime used in that no enhancement in fluidity was detected when the coal size was <45  $\mu$ .

## INTRODUCTION

Coal and pitch carbonisation has previously been investigated using high temperature in-situ  $^1\text{H}$  NMR by Sanada and coworkers <sup>(1)</sup> and, more recently, by Lynch et al, who refer to the technique as "Proton Magnetic Resonance Thermal Analysis" (PMRTA) <sup>(2,3)</sup>. The thermoplastic stage of coal is characterised by a  $^1\text{H}$  NMR signal that consists of a mobile (Lorentzian) and a rigid (Gaussian) component <sup>(2-5)</sup>. The authors recently have used a high temperature Doty NMR probe to rationalise a number of coal carbonisation phenomena, including the effects of particle size and mild oxidation, in terms of both the concentration of rigid and fluid material present, as well as the mobility or  $T_2$  of the later <sup>(4,5)</sup>.

The stabilisation of the plastic phase present during coal carbonisation has been reported to be connected with its hydrogen transfer and donor abilities <sup>(6,7)</sup>. Indeed, aromatic additives that soften upon heating and include coal extracts, pitch and individual polycyclic aromatic compounds can improve fluid properties considerably. For example, using Gieseler fluidity measurements for a series of New Zealand coals, Clemens and Matheson <sup>(8)</sup> reported that both decacyclene and solvent extracts can improve plasticity development. Fortin and Rouzaud used TEM to view the beneficial effects of N-methyl-2-pyrrolidone and boiling anthracene oil extracts on the formation of coke microtexture <sup>(9)</sup>. Indeed, the addition of coal tar pitch (CTP) to coal blends is widely used as a means of enhancing fluidity in coke production. To rationalise the role of solvent extractable material present on the development of a potentially much larger pool of fluid material, Neavel and Marsh <sup>(10)</sup> proposed a parallel between coal liquefaction and carbonisation. The development of plasticity can be considered as a pseudo liquefaction process, in the sense that the extractable material acts as a hydrogen-donor and transfer agent, stabilising the unstable radical species produced by pyrolytic-reaction pathways. In this study, in-situ high temperature  $^1\text{H}$  NMR has been used here to quantify the interactions between a low-volatile

bituminous coal and both a normal (CTP) and a hydrogen-donor pitch (HDP) obtained from a coal liquefaction process.

## EXPERIMENTAL

Table 1 lists the atomic H/C ratios, aromaticity and softening points for the low volatile Australian coal (20% daf volatile matter,  $R_{o,max}$  of 1.46), the CTP and the HDP investigated. The CTP was obtained by distillation of a coal tar at 380°C and under 125 mm Hg vacuum for 2 hours. The HDP was produced in the liquid British Coal Liquid Solvent Extraction (LSE) process at the Point of Ayr facility, and comprises material boiling above 450°C in the product from the hydrocracker. The coal was ground manually using a mortar and pestle to give <45 and 150-212  $\mu$  fractions. Mixtures of coal and pitch (4:1 w/w) were prepared and stirred for one hour to ensure homogeneous blends were obtained.

The high temperature measurements were carried out using a Doty probe on a Bruker MSL-100 spectrometer as described previously <sup>(4,5)</sup>. Approximately 50 mg of sample was packed in a zirconia container, except for the pitch samples, where only around 30 mg was used due to their high fluidity and the fact that a significant amount of sample distills off below 450°C. The average heating rate was around 4°C min<sup>-1</sup>. Spectra were obtained at a number of different temperatures and fitted to Lorentzian and Gaussian components, as appropriate.

## RESULTS AND DISCUSSION

General aspects Figure 1 compares the peak widths at half height,  $\Delta H_{1/2}$ , at temperatures up to 550°C for the coal, CTP and their mixture (4:1 w/w) with a particle size of 150-212  $\mu$ . The softening process for the coal is similar to other coking coals <sup>(4,5)</sup>; the maximum fluidity at 470°C is reflected by the minimum in  $\Delta H_{1/2}$ , corresponding to a maximum in  $T_2$ . During the fluidity range, the peak width of the plastic phase (this dominates  $\Delta H_{1/2}$ ) is only 20-35% of that for the initial coal. At maximum fluidity, the fluid phase accounts for 26% of the hydrogen observed (Table 2). After the onset of resolidification at 490°C, the peak width increases to reach a value similar to that of the initial coal. As anticipated for the CTP, the overall  $\Delta H_{1/2}$  decreases markedly after softening at ca. 190°C and then stays constant close to 1000 Hz (Figure 1). Indeed, as discussed later, the overall peak width of only 10 ppm for both pitch samples means that aromatic and aliphatic hydrogen peaks are resolved. No rigid material was observed in the spectra of the pitch samples above their softening points.

Particle size effect Figure 1 shows that for the peak width for the coal (150-212  $\mu$ )/CTP mixture below 350°C is dominated by the softening of the pitch. For the mixture, the  $\Delta H_{1/2}$  of ca. 1100 Hz is the same as for the pitch alone indicating that the coal particles do not impair the motion of the pitch constituents. In contrast, for the mixture with <45  $\mu$  particles, the  $\Delta H_{1/2}$  (ca. 10 kHz) is nearly ten times larger between 200 and 400°C. This difference in halfwidth is also apparent in the <sup>1</sup>H NMR spectra obtained at maximum fluidity (460°C) for the two mixtures (Figure 2). The increase in peak halfwidth with decreasing particle size has previously been reported as playing an important role in fluidity development <sup>(4,5)</sup>. The mobility or  $T_2$  of the fluid material falls with decreasing particle size, but the amount of fluid material remains constant. These findings suggest that the fluid material - both pitch and coal extract - is weakly adsorbed on the coal and the extent of this interaction increases with decreasing particle size as more of the surface becomes available.

Synergism with coal tar pitch In order to ascertain whether there was any synergism between coal and CTP in terms of plasticity development, the spectra obtained at maximum fluidity were deconvoluted to derive the proportions of fluid and rigid material. The observed and predicted values for the proportion of

hydrogen in the fluid phase are listed in Table 2. The latter were derived from the amounts of fluid material generated when the coal and CTP were heated separately, the hydrogen contents of the coal and CTP and the hydrogen lost during the heating. For the smaller particle size ( $<45\ \mu$ ), the predicted value of 37% is extremely close that of 38% for the proportion of fluid hydrogen at maximum fluidity, indicating no synergism has occurred. In contrast, the predicted proportion of 37% for the fluid hydrogen was significantly lower than that of 45% observed with the larger particle size (150-212  $\mu$ , Table 2). This difference corresponds to an enhancement of 20% in the amount of fluid material generated (Table 2). The same treatment at 400°C indicates that the enhancement in fluidity is 15%, although the total concentration is only about two-thirds that observed at 450°C (Table 2). Thus, a synergistic effect is evident only when the coal particles are sufficiently large (ie. 150-212  $\mu$ ) so as not to impair the motion of the pitch.

**Hydrogen-donor pitch** The structural differences of the two pitches are listed in Table 1, the HDP having a higher atomic H/C ratio and lower carbon aromaticity (0.75 compared to 0.99 for the CTP). Figure 3 presents the  $^1\text{H}$  NMR spectra for the two pitches obtained in the fluid stage at 300°C before any significant proton weight loss. Both pitches display two peaks from aromatic (5-10 ppm) and aliphatic (0-5 ppm) hydrogen, respectively. As expected from the relatively low aromaticity, the HDP spectrum is dominated by the aliphatic peak.

The amount of fluid material generated at 460°C from the coal (150-212  $\mu$ )/HDP mixture is 44% (Table 2), indicating a positive interaction as for the coal/CTP mixture. However, since the HDP loses more weight during the heating process (ca. 60% of its hydrogen) than the more aromatic CTP (only 25%), the degree of synergism is larger with 30% more fluid material being generated than predicted (Table 2). By 400°C, 90% of the fluid phase concentration observed at maximum fluidity (460°C) has already been generated, corresponding to an enhancement of 50% over that predicted. Thus, the HDP extends the range of high fluidity to a significant degree. Moreover, the halfwidths of the fluid components at maximum fluidity for the coal (150-212  $\mu$ )/pitch mixtures (Table 3) indicate that the HDP also mobilises the fluid phase to a much greater extent than the CTP, further demonstrating the ability of this pitch to solubilise the coal.

## CONCLUSIONS

This study has confirmed the ability of high temperature  $^1\text{H}$  NMR to quantify the enhancement of coal fluidity by pitch additives. Particle size appears to be a dominant factor with slow heating, in that positive interactions were not detected with the  $<45\ \mu$  coal fraction. The synergistic effect observed with the HDP was considerably larger than that with the normal CTP, particularly at temperatures below maximum fluidity with the proportion of fluid material being 50% more than that predicted at 400°C.

## ACKNOWLEDGEMENTS

The authors thank the European Coal & Steel Community (Contract No. 7220-EC/870) and the Basque Government (studentship for M.M. Maroto-Valer) for financial support. We are also grateful to British Steel and CRE for supplying the coal and HDP, respectively.

## LITERATURE CITED

- 1 K. Miyazawa, T. Yokono and Y. Sanada, Carbon, 1979, 17, 223.
- 2 L.J. Lynch and D.S. Webster, American Chemical Society Symposium Series, 1983, 230, 353.

- 3 L.J. Lynch, D.S. Webster, R. Sakurovs, W.A. Barton and T.P. Maher, Fuel, 1988, **67**, 579.
- 4 M.M. Maroto-Valer, J.M. Andrésen and C.E. Snape, Prep. Am. Chem. Soc., Division of Fuel Chemistry, 1996, **41**, 1147.
- 5 M.M. Maroto-Valer, J.M. Andrésen and C.E. Snape, Energy & Fuels, in press.
- 6 R.C. Neavel, in Coal Science, vol 1, M.L. Gorbaty, J.W. Larsen, and I. Wender, 1982, Academic Press.
- 7 T. Yokono, T. Obara, Y. Sanada, 1984, Carbon, **22**, 2, 169.
- 8 A.H. Clemens, and T.W. Matheson, 1992, Fuel, **71**, 193, and 1995, Fuel, **74**, 57.
- 9 F. Fortin and J.N. Rouzaud, 1993, Fuel, **72**, 245, and 1994, Fuel, **73**, 795.
- 10 H. Marsh and R.C. Neavel, 1980, Fuel, **59**, 511.

Table 1 Atomic H/C ratios, aromaticities and softening points for the coal and pitches investigated.

	Atomic H/C	Aromaticity <sup>a</sup>	Softening point / °C
Coal	0.61	0.89	470 <sup>b</sup>
Coal tar pitch (CTP)	0.49	0.99	190
Hydrogen donor pitch (HDP)	0.78	0.75	175

<sup>a</sup> The aromaticity fraction was determined by using the quantitative <sup>13</sup>C NMR SPE methodology.

<sup>b</sup> The softening temperature for the coal refers to the maximum fluidity temperature as determined by the standard Gieseler plastometer.

Table 2 Proportion of the fluid component at maximum fluidity temperature for the coal, pitches and coal/pitch mixtures (4:1 w/w).

	Observed mobile H / %		Weight average mobile H / %		Enhancement	
	400°C	460°C	400°C	460°C	400°C	460°C
Coal	12	26	10 / 10 <sup>a</sup>	22 / 23 <sup>a</sup>		
CTP	100	100	16	15		
HDP	100	100	17	11		
Coal (<45 μ) / CTP	27	38	26	37	NONE	NONE
Coal (150-212 μ) / CTP	31	45	26	37	15 %	20 %
Coal (150-212 μ) / HDP	41	44	27	34	50 %	30 %

<sup>a</sup> The first and second values are for the coal in the coal/CTP and coal/HDP mixtures, respectively.

Table 3 Peak widths at half height,  $\Delta H_{1/2}$ , of the fluid component at maximum fluidity for the coal, pitches and coal/pitch mixtures (4:1 w/w).

	Observed $\Delta H_{1/2}$ / Hz	Calculated $\Delta H_{1/2}$ for mixtures / Hz	Enhancement
Coal	5260		
CTP	1000 <sup>a</sup>		
HDP	1000 <sup>a</sup>		
Coal (150-212 μ) / CTP	3000	4700	36%
Coal (150-212 μ) / HDP	1920	4800	60%

<sup>a</sup> Peak width is for aromatic and aliphatic hydrogen bands combined, each band having a  $\Delta H_{1/2}$  of only 300-400 Hz.

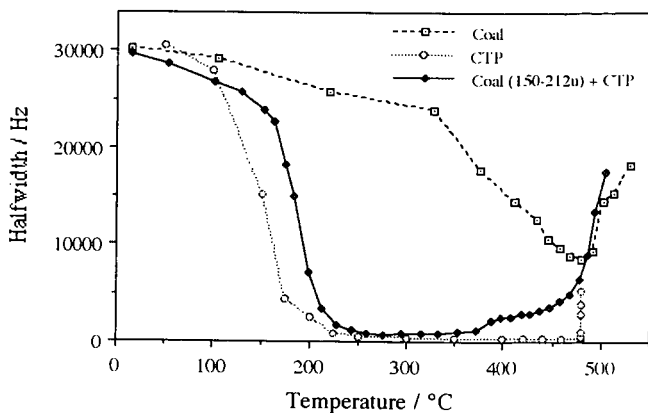


Figure 1 Evolution of the peak halfwidth for the coal (150-212  $\mu$ ), CTP and the coal / CTP mixture.

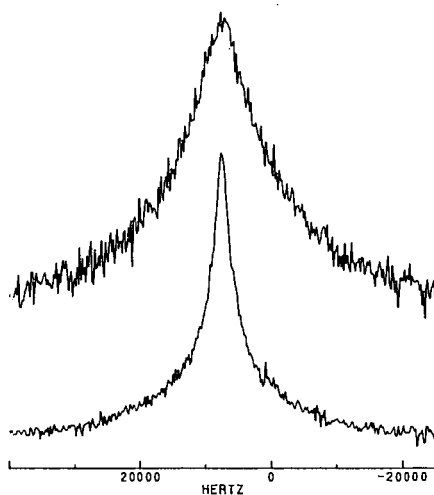


Figure 2  $^1\text{H}$  NMR spectra at maximum fluidity (460°C) for the coal / coal tar pitch mixtures (4:1), coal particle size <45  $\mu$  (top) and 150-212  $\mu$  (bottom).

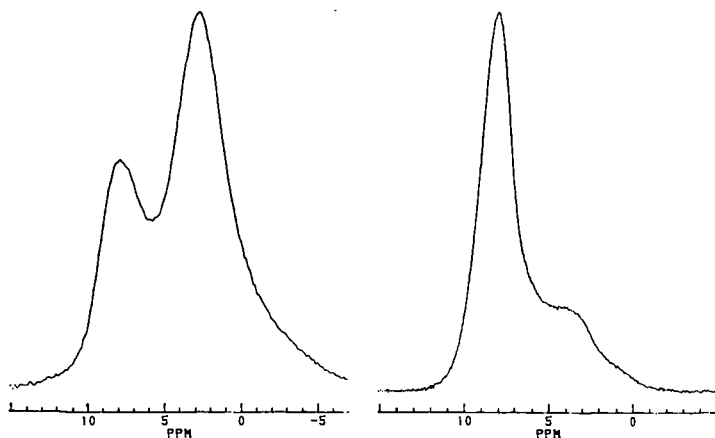


Figure 3  $^1\text{H}$  NMR spectra at 300°C prior to significant weight loss for the CTP (right), and HDP (left).